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(54) **Carrier material for electrophotographic developers.**

(57) An electrophotographic carrier material comprising a spherical core of hematite-containing magnetite and a resinous coating layer applied thereon is provided. The carrier material exhibits good copying characteristics, an improved durability and an enhanced stability to the environmental factors such as humidity. The carrier material may have an appropriate electrical resistivity by virtue of the presence of the hematite and the resinous coating layer.

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CARRIER MATERIAL FOR ELECTROPHOTOGRAPHIC DEVELOPERS

This invention relates to carrier material for electrophotographic developers, in particular two-component developers comprising a toner with a carrier. In particular, the invention relates to a carrier material for electrophotographic developers which comprises a substantially spherical core material consisting essentially of hematite-containing magnetite and having a resinous layer coated thereon.

In electrophotography, the electrostatic image formed on the photoconductor is developed by the magnetic brush method using either a so called "one-component" developer or a "two-component" developer. Usually, the two-component developer system comprises a mixture of relatively fine particles of a toner and relatively coarse particles of a carrier. The toner particles are held on the carrier particles by the electrostatic forces of opposite polarities which are generated by friction of the particles. When the developer comes into contact with an electrostatic latent image formed on the photosensitive plate, the toner particles are attracted by the image and thus make the latter visible. The thus developed image is then transferred onto a recording medium, such as a paper sheet. In the process, therefore, the toner particles should be charged with an accurately controlled amount of static electricity so that they are preferentially attracted to the electrostatically imaged area of the photosensitive plate.

Thus, in turn, the carrier which is used in combination with the toner should fulfil the following criteria: The carrier should have an appropriate triboelectric property which enables it to electrostatically hold the toner particles and to transfer the held toner particles to the electrostatic latent image on the photosensitive plate when contacted. The carrier should have a sufficient mechanical strength to protect the carrier particles from breaking or cracking. The carrier particles should exhibit a good fluidity to facilitate their transfer on the sleeve of the magnetic roll in the printing machine and also to facilitate their mixing with the toner. The carrier particles should be uniform in their electric and magnetic properties. The carrier should be stable with respect to changes in the environmental conditions such as temperature and, in particular, humidity. The carrier particles should have a sufficient durability to ensure an acceptable lifetime.

Although the quality of copies developed by electrophotographic processes is largely governed by the type of copying machine employed, in particular the type of the developing process on which the copying machine is based, it is also known that the copy quality is affected to a significant extent by the developer used therein.

Therefore, various attempts to improve the carrier and toner materials constituting the developers have been made to ensure exact reproduction of an original.

Hitherto, carriers have been selected from a variety of materials. An example which has been most widely used is an iron (metallic) powder of irregular particulate form or shape. Because the iron powder has a high level of saturation magnetization and anisotropy, the magnetic brush (i.e. a tuft of filaments comprising the carrier particles having the toner particles theron, each of the filaments being generally formed with the carrier particles chained together in one length by the magnetic forces generated by and transferred from the magnetoroll, and each filament standing on end from the surface of the sleeve of the magnetoroll) is necessarily longer and more firm than those obtained with other carrier materials of a lower saturation magnetization. This phenomenon may be often observed where the iron powder carrier is of a flat and irregular particulate shape. If the magnetic brush is long and firm, the density of the brush tuft will be low and hence it is difficult to produce a fine copy having a good gradient. In spite of the poor gradient of copy achieved by a developer comprising the iron powder carrier of irregular particulate shape, such a developer may be advantageous in that it is possible to generate a high degree of chromic density therewith. Therefore, this type of developer has been employed in a type of copying machine which is provided with a relatively wide clearance between the surface of the sleeve of the magnetoroll and the surface of the photoconductor.

On the other hand, in order to develop a fine copy of an improved gradient, a carrier comprising an iron powder of a spherical particulate shape has been employed. Since the iron particles are spherical and, thus, isotropic, the disadvantages which are caused by the anisotropy of the carrier comprising the irregularly shaped iron powder are significantly reduced by use of the spherical iron carrier. The magnetic brushes formed therefrom are remarkedly short and dense. Accordingly, the developing torque required is also reduced. However, this spherical iron powder is not completely satisfactory; since the carrier again comprises me-

tallic iron and has a relatively high specific gravity and hence a relatively large apparent density (usually greater than 4.0 g/cm^3), the particles tend to jump or fly away and to cause difficulties in the process and machine. To prevent the escape of the particles, it is necessary to adopt a special and complicated design for the magnetoroll and related parts of the copying machine. Further, the heavy iron carrier may give rise to a high stress on the toner particles when admixed together and may adversely affect the working life of the developer. With this type of carrier, although it is possible to develop a relatively high quality of copies having an improved gradient, the copies generally tend to have a relatively low degree of chromic density. This undesirable tendency has been reduced or removed by appropriate modifications of the machine or by regulation thereof, for example, by increasing the electrostatic potential charged on the surface of the photoconductor.

It has been proposed to use ferrite, an oxidic ferromagnetic material, as a carrier material in an attempt to improve the copy quality and to prolong the working life of developer. Because the ferrite carrier has a saturation magnetization (about 40-70 emu/g) lower than that of iron powder (about 200 emu/g), the magnetic brush formed from the former is soft and thus fine copies of an improved gradient may be developed therewith. Further the ferrite carrier is advantageous in that the stress exerted on the toner particles is significantly reduced and consequently the durability of developer is prolonged, since the ferrite carrier has a specific gravity lower than that of metallic iron. The developing torque required is also reduced. Notwithstanding the above advantages, the ferrite carrier is used only within a limited range of application, because the electrical resistivity of ferrite is rather high. Further the ferrite material is relatively sensitive to environmental conditions so that the performance of the ferrite carrier tends to be significantly influenced by such changes in the environmental conditions as humidity variations and the resulting copy quality tends to change over the period of operation in which the ferrite carrier is used.

To improve the environmental stability of the ferrite carrier, it has been proposed that the ferrite carrier particles be provided with a resinous coating layer, although this further increases the undesirably high electrical resistivity of the material, resulting in a further limitation of the application range and additional production costs.

An object of the present invention is to provide a novel carrier material with which the problems associated with the known carriers are obviated or substantially removed.

Another object of the invention is to provide methods for preparing this novel carrier.

A further object of the invention is to provide a novel carrier which is effective in producing electrophotographic copies of excellent quality, is stable in respective of changes in environmental conditions, and has increased durability.

Accordingly, the present invention provides a carrier material for electrophotographic developers which comprises a substantially spherical core particle consisting of hematite-containing magnetite and having a resinous layer coated thereon.

The carrier material of the invention which is made of hematite-containing magnetite has a lower electrical resistivity than ferrite. This low resistivity provides a wide room for increasing the resistivity over a wide range by coating the material with a resinous insulating material. Therefore, it is possible to accommodate the resistivity to various types of copying machines and processes requiring different optimal levels of resistivity with respect to the carrier material.

The spherical shape of the carrier particles provides the carrier with a desirable fluidity.

The present carrier material has a specific gravity lower than iron and an apparent density comparable with that of the ferrite carrier. Therefore, with the present carrier, a relatively low level of developing torque is required in the machine and a satisfactory developer working life is provided.

The present carrier material has a saturation magnetization (σ_s) within the range of about 40 - 80 emu/g similar to that of ferrite and will form a soft and dense magnetic brush resulting in development of a high quality copy. The relatively low saturation magnetization will reduce the torque required for cutting the top of the brush during conveyance of the developer on the magnetic roll and, thus, will contribute to extend the durability of the material.

The hematite-containing magnetite particles which may be used in the present invention may be prepared, for example, in the following manners:

a) A homogeneous aqueous slurry comprising finely divided hematite and magnetite is sprayed in a spray drier to give granules, which are then calcined, lightly ground and classified into a desired size fraction (for example, 20 - 200 μ).

b) Spherical magnetite particles in a desired size range are subjected to partial oxidization.

The carrier material of the invention exhibits a saturation magnetization (σ_s) in the range of about 40 - 80 emu/g. The saturation magnetization may be determined in a magnetometer, for example a sample-vibrating type Magnetometer VSMP-I (ex. Toei Kogyo Co., Japan). It has been found that the present product exhibits maximum saturation magnetization in a magnetic field of about l4.5 KOe.

If σ_s of the particles is less than 40 emu/g, it is difficult to prepare the particles in a homogeneous state. In other words, though it is possible to prepare carrier particles having a value of σ_s as low as about 30 emu/g, the respective particles are not equal to each other in their magnetic properties. On the other hand, if the particles have a σ_s exceeding 80 emu/g, they tend to form an undesirably hard brush on the magnetic roll. In the both cases, the particles are not suitable for the purpose of the invention.

It is preferred that the size of the spherical core particles is in the range of about 30 - 200 μ.

The spherical core particles having the preferred ranges of the physical properties, i.e., a σ_s of 40 - 80 emu/g and a diameter of 30 - 200 μ may be coated by an appropriate resinous material. The resinous material may be applied to the core particles as a solution in an organic solvent, such as methyl ethyl ketone, xylene, n-butanol, methyl cyclohexane or toluene. The resinous solution may be applied to the core particles, for example, by dipping the particles in the solution or spraying the solution over a fluidized mass of the core particles. When a thermosetting resin is employed, the coated particles are subjected to a suitable heat treatment to give the resin-coated carrier material. Any resin may be used in the preparation of the carrier material of the present invention provided that it is effectively soluble in the common solvents.

The amount of the resinous material to be applied to the core material is governed by the nature of the resin employed and the type of copying machine (and hence the electrostatic and electrical resistivity properties suitable for the particle machine) for which the product carrier is to be supplied. Generally, the amount of resin suitable for the purpose of the invention will be in the range of 0.5 - 8%, preferably 1.5 - 6% by weight.

The resin-coated carrier material according to the present invention may be used in conjunction with conventional toners such as those, for example, made from a natural resin, a synthetic resin, a blend of natural and synthetic resins or such a material modified by incorporation of any appropriate additives.

Examples

The invention will be illustrated with reference to the following non-limiting Examples.

Example 1

To 100 parts of magnetite powder, 30 parts of hematite powder was added (by weight). The mixture charged into a wet attrition mill and mixed thoroughly to give a homogeneous aqueous slurry. Then the slurry was dried in a spray-drier to form spherical granules of 30 - 150μ in diameter. The granules were calcined at about 1200°C for about 2 hours in a nitrogen atmosphere and allowed to cool. The calcined mass was lightly ground and classified to give a fraction of 75 - 150 μ in diameter.

The thus prepared spherical particles containing magnetite and hematite exhibited a saturation magnetization (σ_s) of 60 emu/g.

To 10 kg of the hematite-containing magnetite particles, 2 kg of a solution of a styrene/acryl copolymer resin ("MH 7015" produced by Fujikura Chemicals Co., Ltd.) in toluene (a resin content of 10%) was spray-coated to give a resin-coated carrier material according to the invention.

The carrier was mingled with a commercially available toner for magnetic brush development (a negatively chargeable toner adapted for use in "Xerox 3870" machine). The thus obtained developer was used for developing an electrostatic latent image formed on a selenium photoconductive surface to obtain a high quality copy showing an excellent reproducibility in the intermediate tone range. It was found that the initial copy quality was substantially maintained even after reproduction of 60,000 copies.

Example 2

An aqueous slurry of magnetite powder was spray-dried in a spray drier to give spherical particles of 30 - 150 μ in diameter. After about 2 hours of calcination at about 1200°C in a nitrogen atmosphere, the product was cooled, lightly ground and classified to give a fraction of 75 - 150 μ in diameter.

The spherical magnetite particles were heat treated at 300°C in a rotary kiln for 3 hours in air. Spherical hematite-containing magnetite particles formed by partial oxidation of the magnetite.

The obtained spherical hematite-containing magnetite particles had a saturation magnetization of 45 emu/g.

To l0 kg of the spherical powder, l kg of the same resin solution as in Example l was spray coated to give a carrier powder according to the invention.

In the same manner as in Example l, a developer was prepared. Using this developer, an electrostatic latent image on a selenium photoconductive surface was developed, with a high quality copy of a good intermediate tone. No substantial changes were seen in the copy quality after as many as 60,000 times of development.

Comparative Example l

An aqueous slurry of magnetite powder was spray-dried in a spray drier to give spherical particles of 30 - l50 μ in diameter. After about 2 hours of calcination at about l200°C in an nitrogen atmosphere, the product was cooled, lightly ground and classified to give a powder of 75 - l50 μ in diameter.

The resulting spherical magnetite particles had a saturation magnetization of 86 emu/g.

The powder was coated in the similar manner to that in Example l.

The resulting carrier powder was used to prepare a developer in the same manner as in Example l. The developer was subjected to the copying test as described in Example l. The resulting copy showed a high contrast with a poor intermediate tone. The results were poor than those of Examples l and 2.

Comparative Example 2

An aqueous slurry of magnetite powder was spray-dried in a spray drier to give spherical particles of 30 - l50 μ in diameter. After about 2 hours of calcination at about l200°C in a nitrogen atmosphere, the product was cooled, lightly ground and classified to give a powder of 40 - 75 μ in diameter.

The spherical magnetite particles were heat treated at 800°C in a rotary kiln for 2.5 hours in air to give spherical particles of hematite-containing magnetite.

The obtained spherical particles of hematite-containing magnetite had a saturation magnetization of 35 emu/g.

The spherical particle powder of hematite-containing magnetite (l0 kg) was coated with l.5 kg of a solution of acryl resin ("BR83" produced by Mitsubishi Rayon Co., Ltd.) in toluene (resin content: 6%) by spraying technique.

The thus-obtained carrier powder was mixed with a toner for magnetic brush development (negatively-chargeable toner, "BD88ll" produced by Toshiba Electric Co., Ltd.) to prepare a developer, with which an electric latent image on a selenium photosensitive member was developed. An accidental carrier deposition on the photoconductive surface occurred. With such an accident, the carrier could not be put into practical use.

The carrier material produced in this comparative example exhibited a saturation magnetization in the range of as low as l5 - 25 emu/g.

Example 3

An aqueous slurry of magnetite powder was spray-dried in a spray drier to give spherical particles of 30 - l50 μ in diameter. After about 2 hours of calcination at about l200°C in a nitrogen atmosphere, the product was cooled, lightly ground and classified to give a powder of 40 - 75 μ in diameter.

The spherical magnetite particles were heat treated at 400°C for 30 minutes to give spherical particles of hematite-containing magnetite.

The obtained spherical particles of hematite-containing magnetite had a saturation magnetization of 73 emu/g.

The spherical particle powder magnetite (l0 kg) was coated with 2.5 kg of a solution of acryl resin ("BR83" produced by Mitsubishi Rayon Co., Ltd.) in toluene (resin content: 6%) by spraying technique.

The thus-obtained carrier powder was mixed with a toner for magnetic brush development (negatively-chargeable toner, "BD88ll" produced by Toshiba Electric Co., Ltd.) to prepare a developer, with which an electric latent image on a selenium photosensitive member was developed. An high quality copy with a relatively good intermediate tone was reproduced.

Claims

l. A carrier material for electrophotographic developers which comprises a substantially spherical core particle consisting of hematite-containing magnetite and having a resinous layer coated thereon.

2. A carrier material as claimed in Claim l which has a saturation magnetization of 40 - 80 emu/g.

3. A carrier material as claimed in Claim l or 2 which has a particle size in the range of 30 - 200 μ.

4. A method for preparing the carrier material as claimed in any one of the preceding claims which comprises the steps of:

providing core particles comprising hematite-containing magnetite and which are substantially spherical;

and

coating the spherical core particles with a resinous material.

5. A method as claimed in Claim 4 in which the core particles are formed from an intimate mixture of powdered hematite and magnetite.

6. A method as claimed in Claim 4 in which the core particles are prepared by partially oxidizing spherical magnetite particles.

7. An electrophotographic developer comprising a toner powder and the carrier material according to any one of Claims l, 2 and 3 or the product obtained by the method according to any one of Claims 4, 5 and 6.